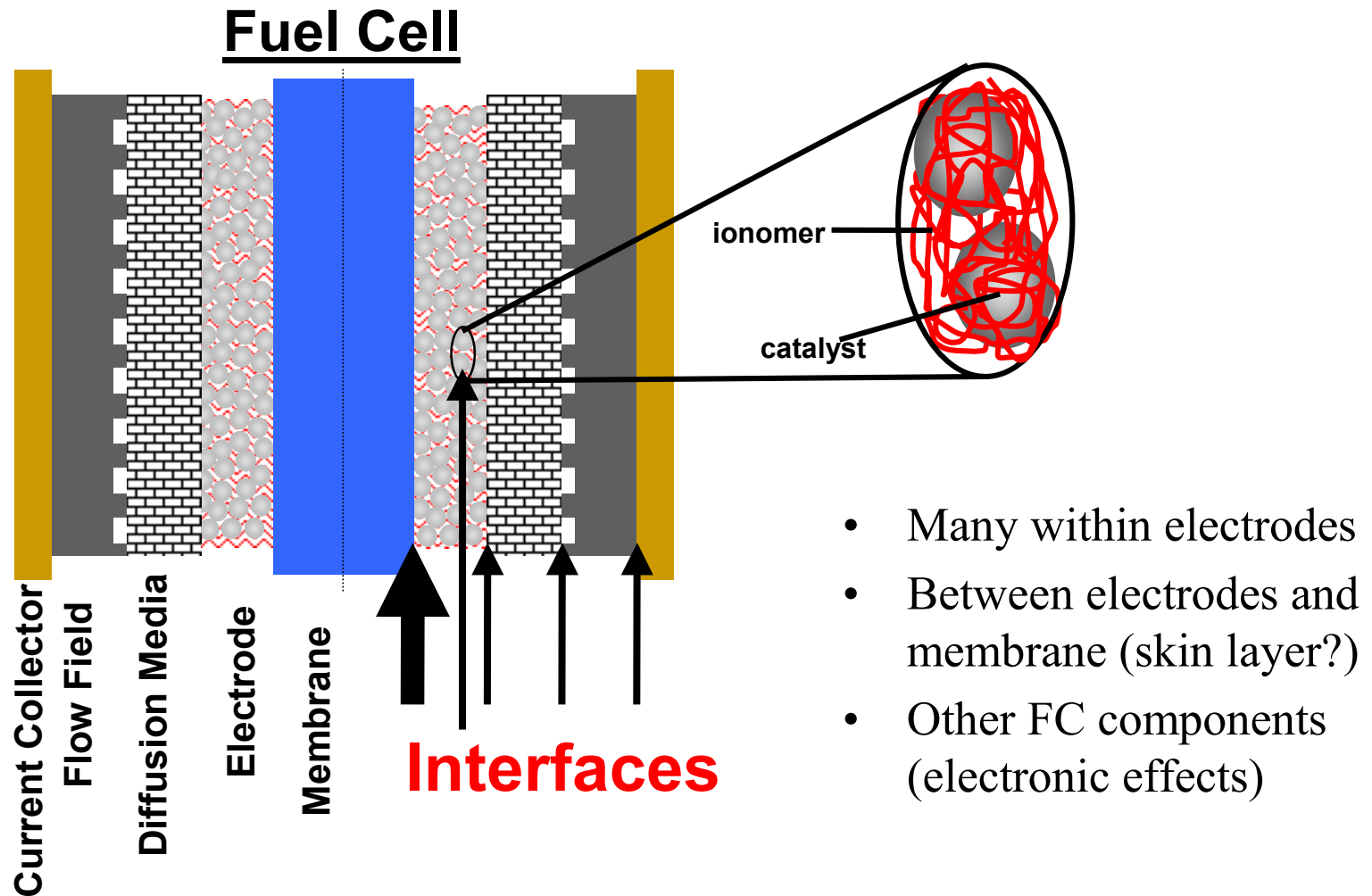


MEA and Interfacial Issues in Low Temperature Fuel Cells

Bryan Pivovar

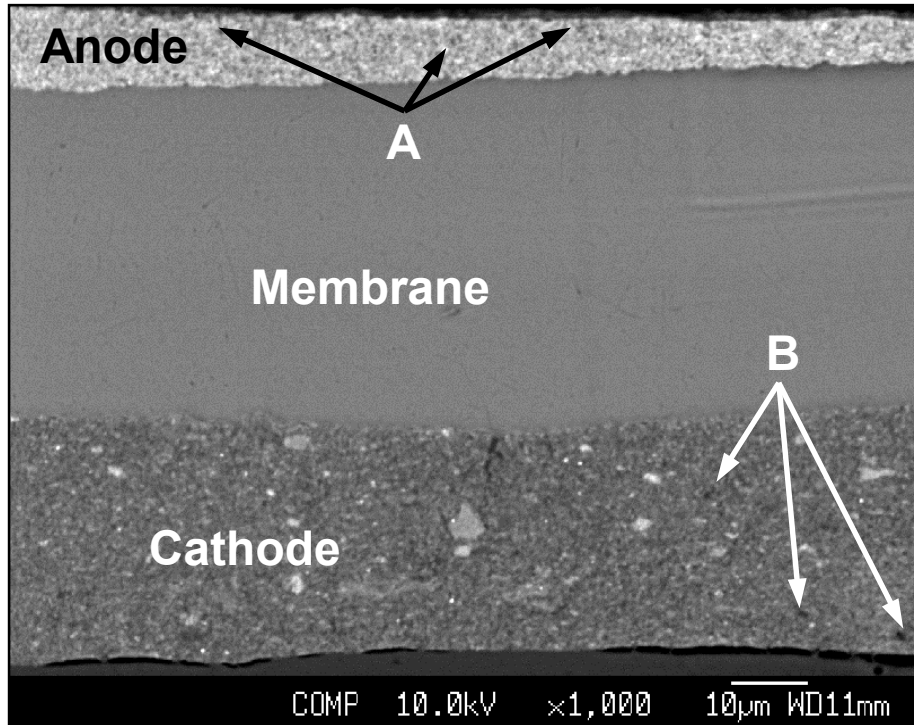
Los Alamos National Laboratory

Interfaces in a Fuel Cell

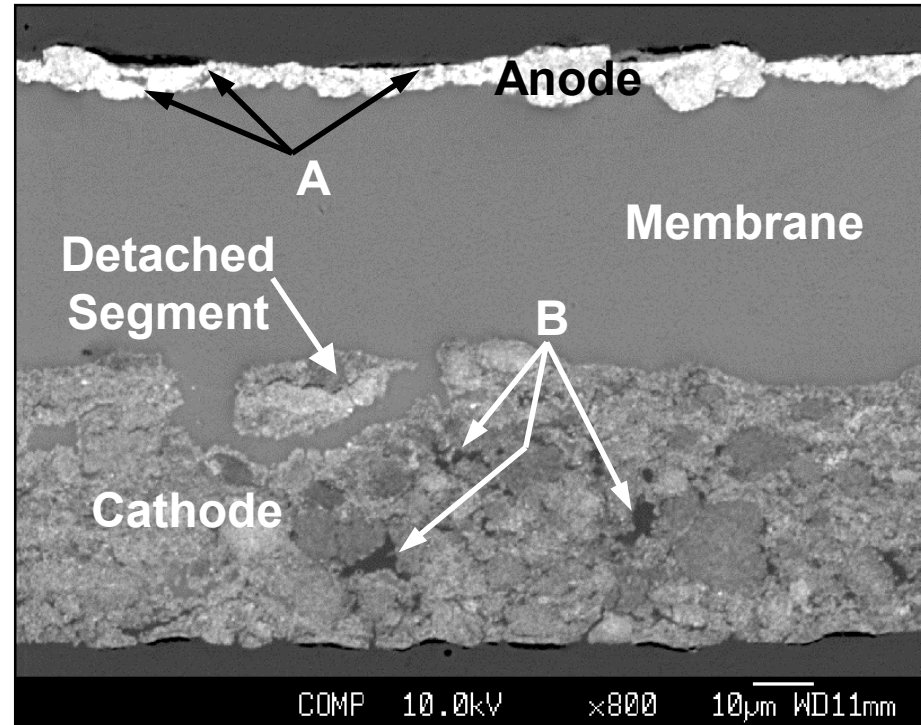


SEM Pictures Comparing MEA Cross-Section Before/After ~2200 Durability Test

Cryogenic Sectioning with $N_2(l)$ Used to Obtain MEA Cross-Sections



- Relatively uniform catalyst layer compositions & thicknesses.

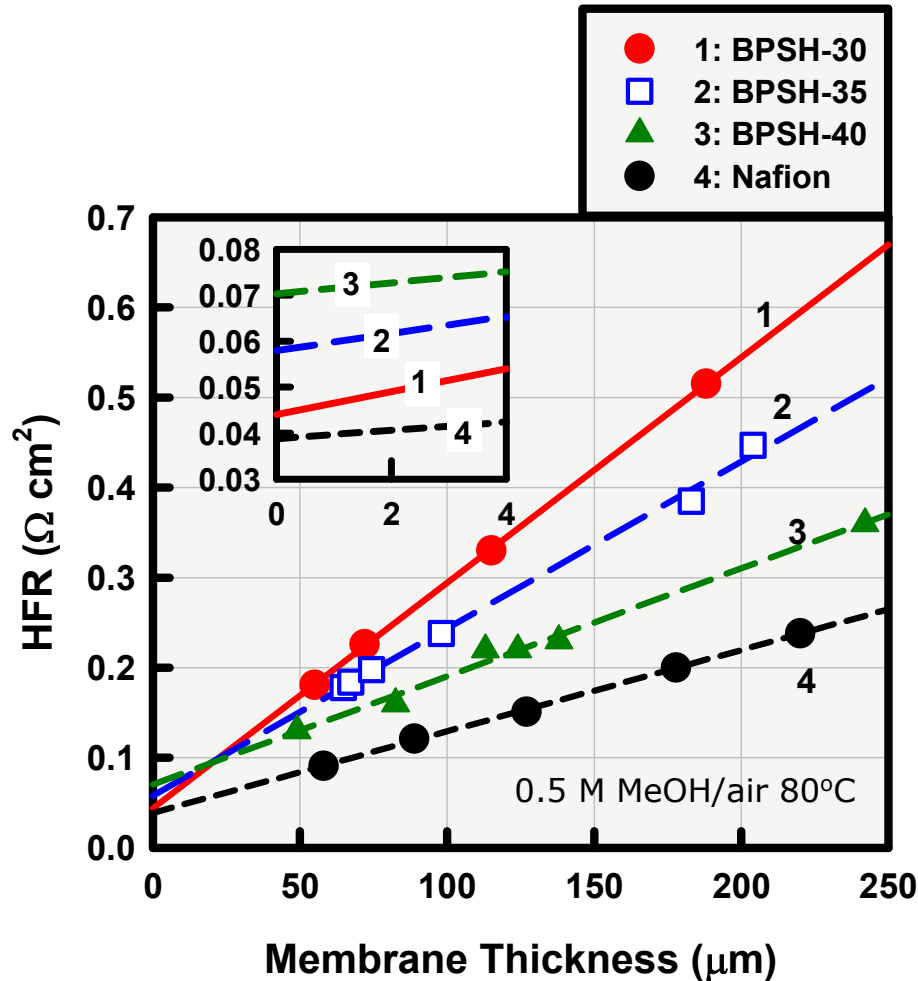


- Significant deterioration of catalyst layer compositions & structures.
- Decrease in thickness uniformity of catalyst layers.

*Wood et. al., 206th Meeting of The Electrochemical Society, Honolulu, Hawaii, October 5th, 2004

Workshop on Sub-Freezing Effects
February 1, 2005

Membrane – Electrode Interface



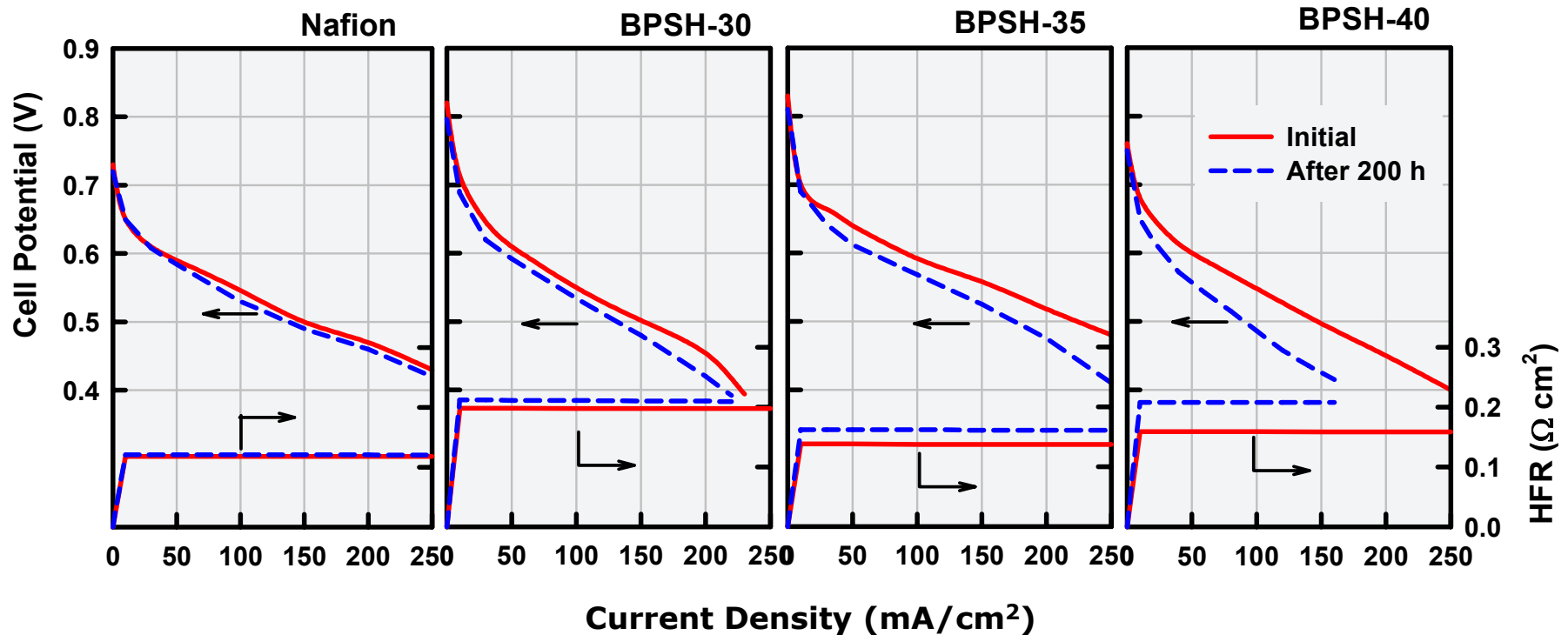
**Conductivity, σ ,
Interfacial Resistance, $R_{interface}$**

Membrane	σ (mS/cm)	$R_{interface}$ (m $\Omega \text{ cm}^2$)
BPSH-30	39	16
BPSH-35	54	30
BPSH-40	78	42
Nafion	111	7

$$HFR = R_{non-mem} + R_{mem}(x)$$

$$R_{non-mem} = R_{elec} + R_{int}$$

Influence of Interfacial Compatibility on Longer-Term Performance



7

16

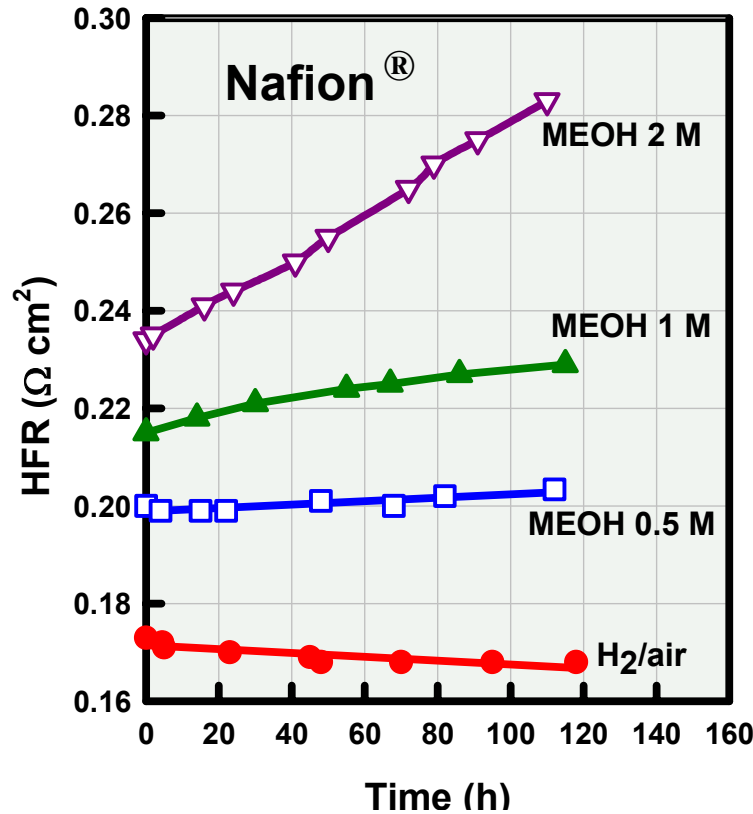
30

42

Interfacial resistances (mΩ cm²)

0.5 M MeOH/air 80°C

Effect of Methanol Feed Concentration on Cell Resistance during Extended-Term Test



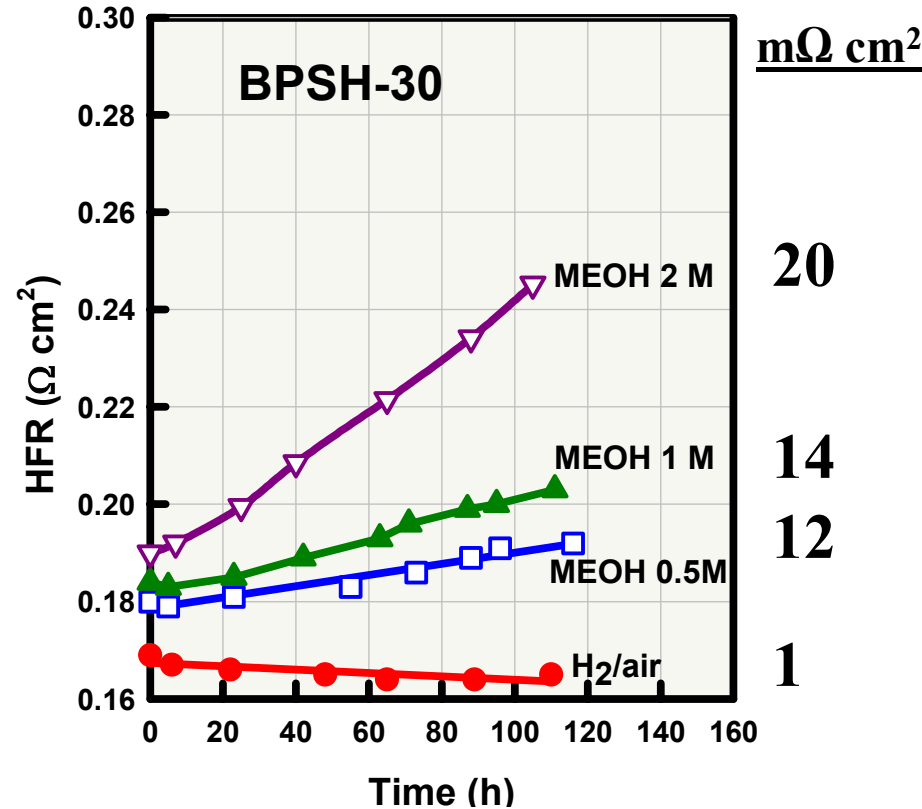
$\text{m}\Omega \text{ cm}^2$

19

13

7

2



$\text{m}\Omega \text{ cm}^2$

20

14

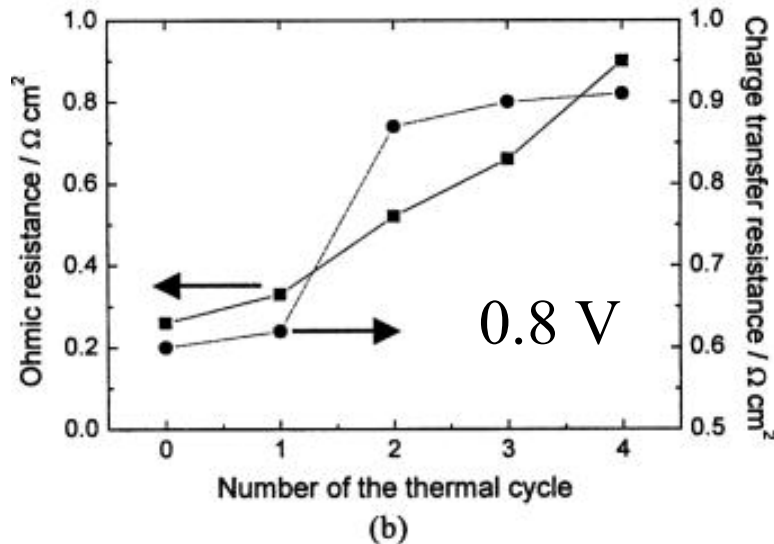
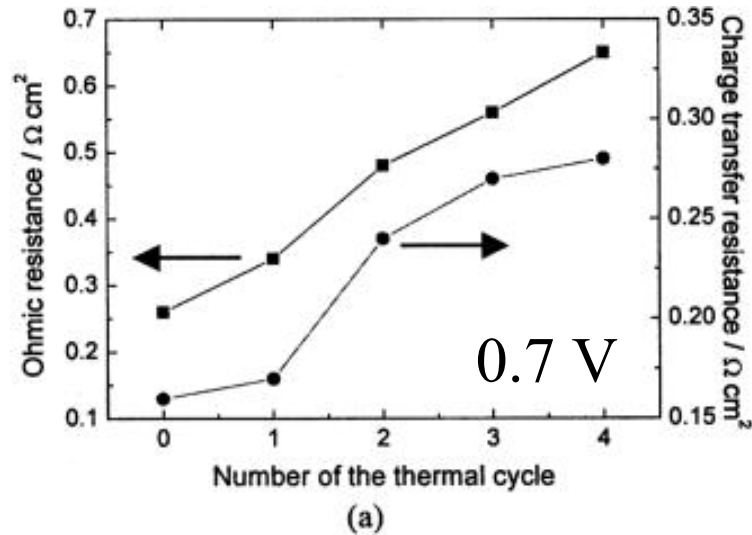
12

1

Correlated Factors:

Initial Interfacial Resistance, HFR gain, performance loss

Literature Degradation: Interfacial Failure?

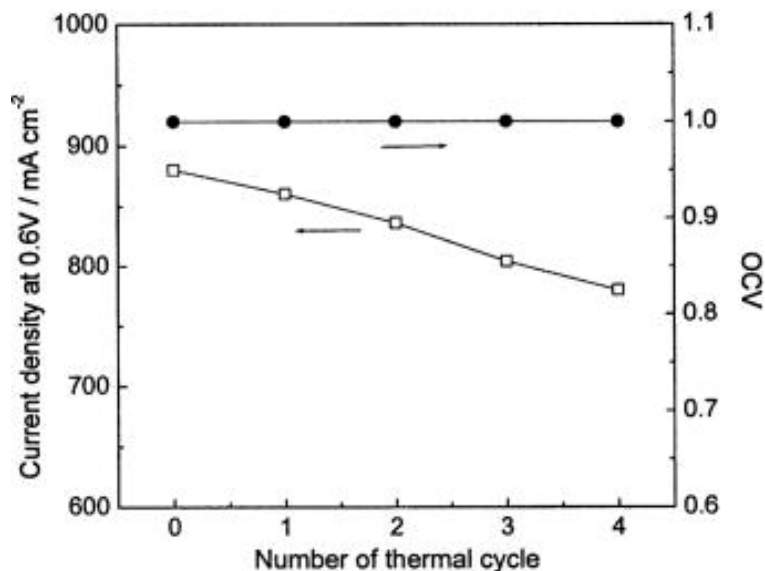


- Membrane resistance was not changed after thermal cycling
- Increased resistance most likely due to interfacial losses

Ref. Cho et. al. *J. Electrochem. Soc.* **150**, A1667 (2003)

Performance degradation after freezing/thawing cycle

✓ **OCV was maintained while current density at 0.6 V decreased.**



Effects of thermal cycles from 80 to -10°C on the OCV and current density measured at a cell voltage of 0.6 V and at a cell temperature of 80°C .

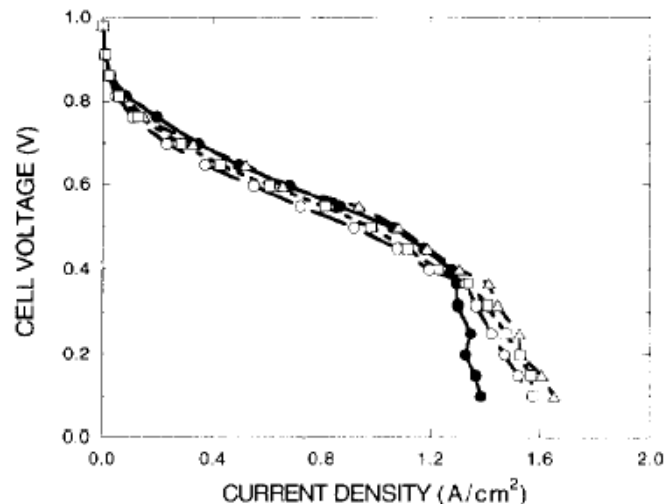


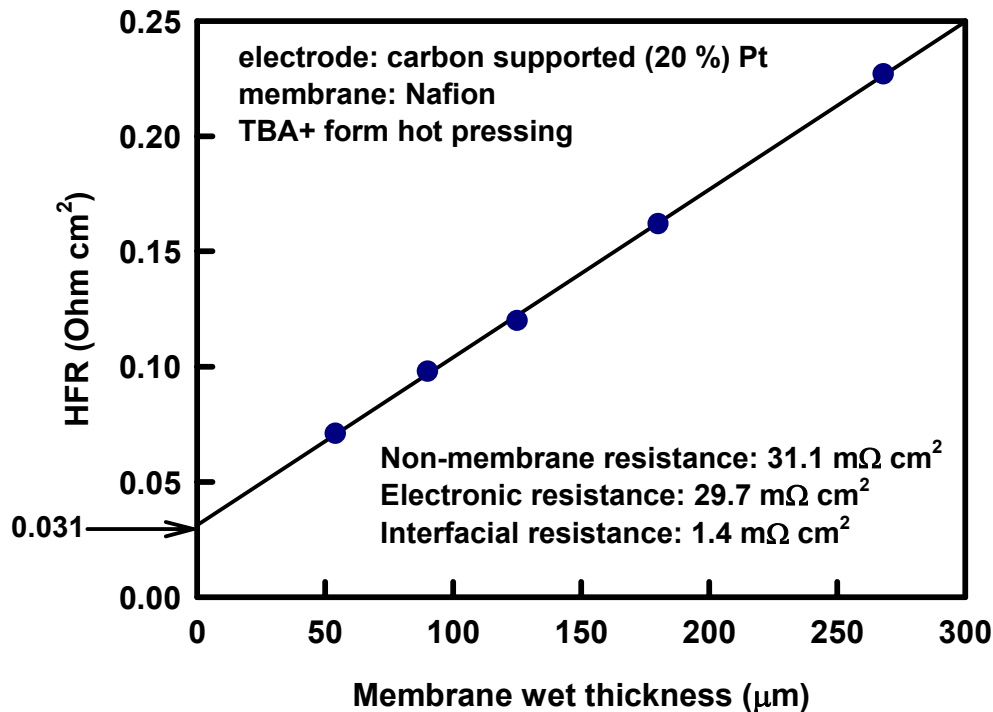
Fig. 12. Effect of several freeze-thaw cycles on the performance of a single cell with TBA^+ thin film catalyst layers. Frozen at -10°C . Operation conditions are the same as in Fig. 2. (●) before freezing, (Δ) after the 1st freeze, (\circ) after the 2nd freeze, and (\square) after the 3rd freeze.

Electrochem. Acta, Wilson et al., **40**, 355, (1995)

Performance discrepancies

Ref. Cho et. al. *J. Electrochem. Soc.* **150**, A1667 (2003)

Interfacial Resistance between Nafion and Carbon Supported Pt Electrode

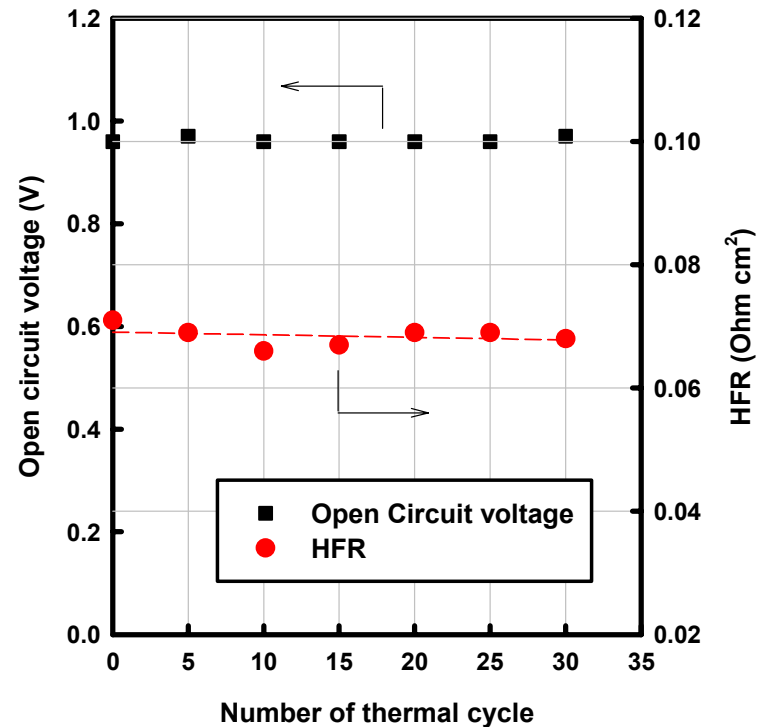
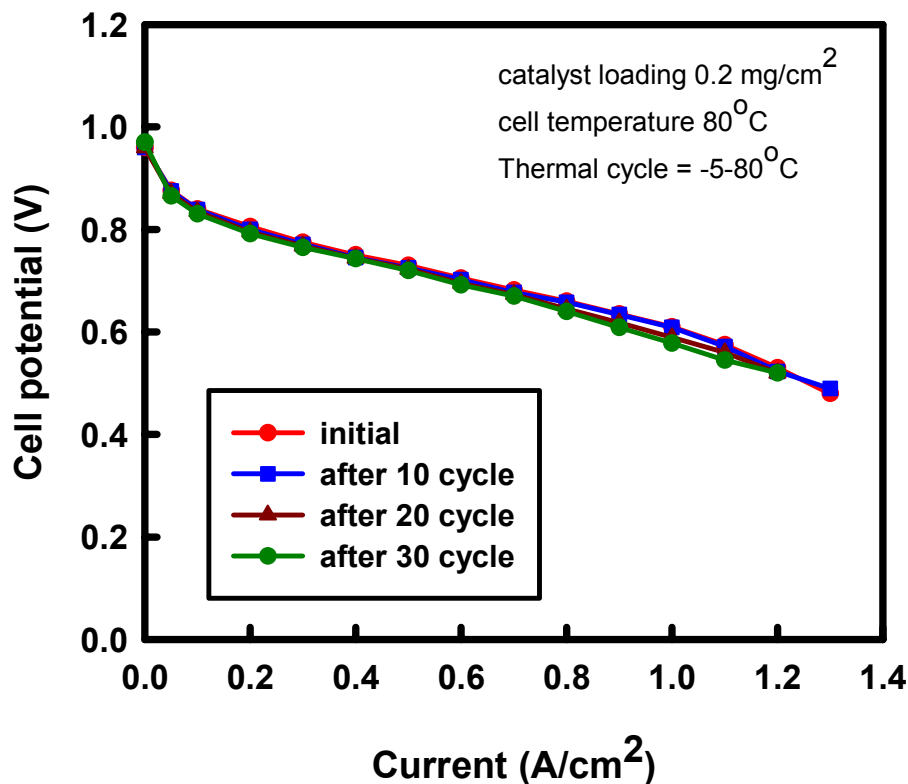


- Interfacial resistance between Pt electrode (20% carbon supported) and Nafion membrane was small ($1.4 \text{ m}\Omega \text{ cm}^2$).

Cell HFR vs. Membrane Thickness

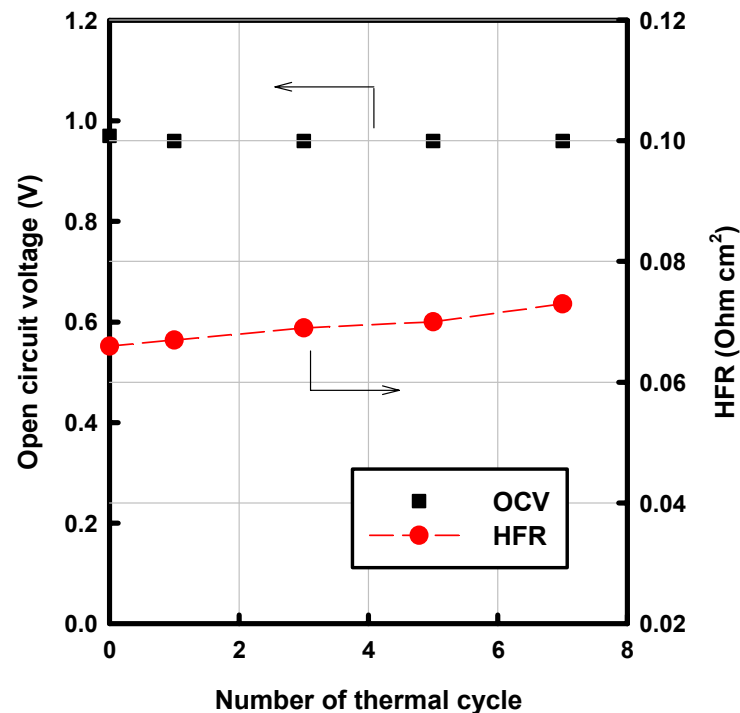
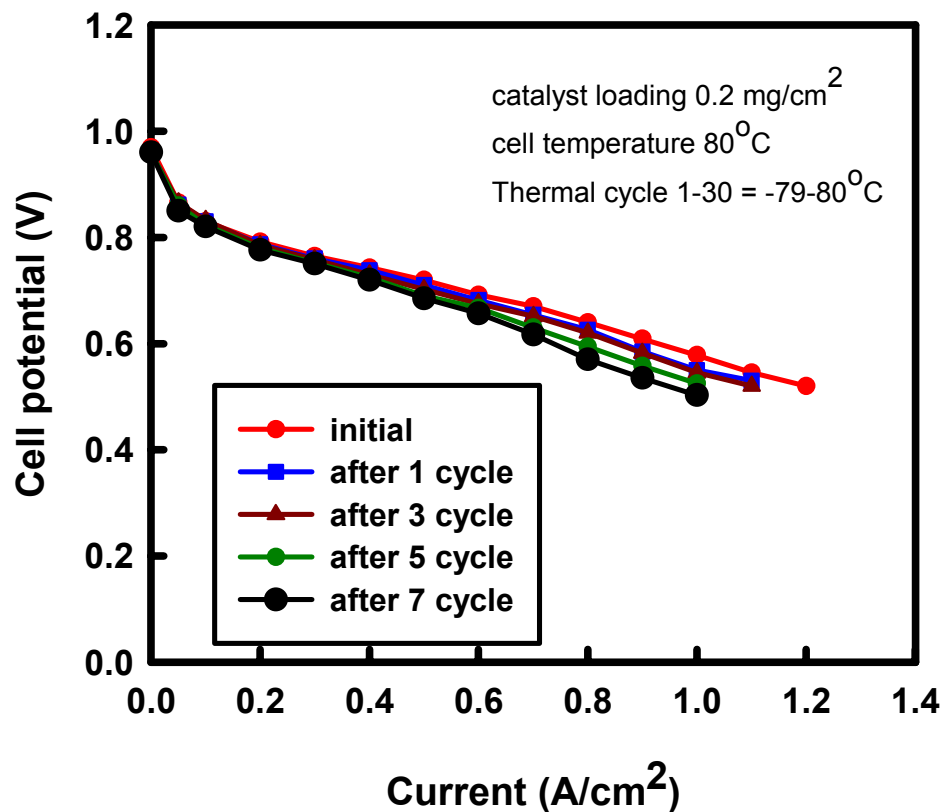
- MEA was fabricated from TBA+ form Nafion solution followed by hot pressing (220°C).

Performance Change after Freeze/thawing Cycle (Temp. cycle = -5-80°C)



- We observed no performance degradation after 30 freeze/thawing cycle ($-5-80^\circ\text{C}$) with stable OCV and HFR.

Performance Change after Freeze/thawing Cycle (Temp. cycle = -79-80°C)



- We observed the noticeable performance decreased after 7 freeze/thawing cycle ($-79-80^\circ\text{C}$) with increasing HFR.

Summary of Results

	<i>Cho et al.</i>	<i>Wilson et al.</i>	<i>This work</i>	
Membrane	Nafion 115	Nafion 112	Nafion 112	
Electrode	20 wt% Pt/C (0.4 mg/cm ²)	20 wt% Pt/C (0.16 mg/cm ²)	20 wt% Pt/C (0.2 mg/cm ²)	
GDL	wet proofed carbon paper	hydrophobic carbon cloth	hydrophobic carbon cloth	
MEA processing	Catalyst ink sprayed on GDL / 140°C hot pressing	Decal painting (TBA ⁺ form catalyst) / 200°C hot pressing	Decal painting (TBA ⁺ form catalyst) / 200°C hot pressing	
F/T cycle	-10 – 80°C (4 cycle)	-10 – 80°C (3 cycle)	-5 – 80°C (30 cycle)	-79 – 80°C (7 cycle)
Results	Performance drop, HFR increase, catalyst loss	No performance loss	No performance loss	Performance drop HFR increase

Influence of MEA processing Conditions

Membrane	Nafion 112		
Electrode	20 wt% Pt/C (0.2 mg/cm ²)		
GDL	hydrophobic carbon cloth	hydrophobic carbon cloth	wet proofed carbon paper
MEA processing	Catalyst ink painted on GDL / 140°C hot pressing	Catalyst ink painted on membrane / 140°C hot pressing	Catalyst ink painted on GDL / 140°C hot pressing
F/T cycle	-5 – 80°C (~10 cycles)		
Results	Preliminary work suggests little effect from GDL choice and MEA processing		

Effect of Conditions

- Material Concerns
 - MEA (prep, composition)
 - GDL
 - Bipolar/End plates
- Operational
 - Water content
 - Temperature (time)